

THE ANALYST.

JULY, 1901.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE monthly meeting of the Society was held on Wednesday evening, June 5, in the Chemical Society's Rooms, Burlington House.

The President (Dr. J. Augustus Voelcker, M.A., B.Sc.) occupied the chair.

The minutes of the previous meeting were read and confirmed.

A certificate of proposal for election to membership in favour of Mr. F. M. Wharton, F.I.C., was read for the second time.

The President announced that it had been arranged that the summer meeting of the Society should be held at Cambridge on Friday, July 19.

The following papers were read: "Arsenic in Coal and Coke," by Alfred C. Chapman; "Public Analysts' Records," by J. F. Liverseege; and "The Use of Partially Sterilized Milk Cultures in judging the Purity of Water," by H. Droop Richmond.

ON THE MAUMENÉ TEST FOR OILS.

By C. AINSWORTH MITCHELL, B.A., F.I.C.

(Read at the Meeting, April 3, 1901.)

IT was pointed out by Mr. Hehner and myself in a paper read before this Society in 1895 (ANALYST, xx., 146) that in certain cases there existed a rough proportion between the percentage of iodine absorbed by an oil and the Maumené figure, but that the factor applicable to different specimens of one kind of oil could not be applied to those of another kind, even when the determinations were made by the same person.

We hazarded the suggestion that, if the other thermal factors could be eliminated or made constant, the heat produced by the absorption of the sulphuric acid would be found to be directly proportional to the degree of unsaturation in the majority of cases.

In the ordinary methods of applying the test, there seems to be but little hope of attaining this end, for when concentrated sulphuric acid is added to an oil there is a strong local action, and it depends on the method and rate of stirring as to how soon a homogeneous mixture is obtained. This has a considerable influence on the rise of temperature.

Then, when highly unsaturated glycerides, like linseed and fish oils, are tested, it is practically impossible to get concordant results, owing to the higher temperatures obtained leading to further action on the part of the sulphuric acid, which it is not possible to keep within limits.

This was recognised by Maumené himself, who met the difficulty by mixing the oil with a definite proportion of olive oil of known thermal value, and subsequently making a correction for the addition.

Ellis (*Journ. Soc. Chem. Ind.*, 1886, 361) employed a mineral oil for the same purpose, but his method was further complicated by the fact that, the rise of temperature with the mineral oil and sulphuric acid alone in the blank determination being too slow, he had to mix the mineral oil with colza oil in order to obtain a more rapid reaction.

Both these methods suffer from the drawbacks of introducing active agents into the reaction, and of there being no possibility of different chemists obtaining diluting agents of exactly the same thermal value. Moreover, they only partially remedy the effects of overheating.

It occurred to me that carbon tetrachloride might be a suitable substance for the dilution, and that, if so, it would be possible for different observers to be sure of working under the same conditions.

On stirring 10 c.c. of carbon tetrachloride with 1 c.c. of sulphuric acid (93.8 per cent.), I found that the rise in temperature only amounted to 0.5° C. after one minute, and that this might be taken as a constant and neglected.

Method.—After some preliminary experiments I adopted the following method, so as to make the test comparable with the bromine thermal test devised by Mr. Hehner and myself: 2 grammes of the oil were weighed into a vacuum-jacketed tube,* 10 c.c. of carbon tetrachloride added, the temperature of the solution taken, and 2 c.c. of sulphuric acid introduced.

The liquid was continually stirred with a standard Jena thermometer graduated in tenths of a degree, and a note taken of the rise in temperature. Shortly before the end of the reaction the sulphonated product separated, and rose to the surface of the carbon tetrachloride. In this way duplicate results could be obtained agreeing within 0.2 of a degree. The time occupied by the reaction was about one minute, but to this point I shall return presently.

Fatty Acids.—I made the first experiments with the fatty acids themselves, so as to eliminate from the reaction the heat due to hydrolysis. In each case I determined the bromine thermal factor by our original method (*ANALYST*, xx., 146), and I give the iodine values calculated from the two thermal values in the subjoined table. The vacuum jacketed tube was standardized on almond oil (Hübl value, 96.5; bromine thermal value, $16.1 \times 6 = 96.5$) and lard (Hübl value, 64.6; bromine thermal value, $10.8 \times 6 = 64.8$).

* These can be obtained from C. E. Müller, High Holborn, W.C.

I.

FATTY ACIDS.

Oil.	Rise with H_2SO_4 (93·8 per cent.). ° C.	Calculated Iodine Value Rise $\times 7$.	Bromine Thermal Rise. ° C.	Calculated Iodine Value Rise $\times 6$.
1. Oleic acid I. (old)	11·8 ; 11·7	82·6	14·0	84·0
2. " II. "	11·3 ; 11·4	79·8	14·3 ; 14·2	85·8
3. Almond	13·6 ; 13·8	96·6	16·1	96·6
4. Earthnut	12·5	87·5	14·2	85·2
5. Olive	11·6	81·2	14·1	84·6
6. Cotton	16·8	117·6	18·1	108·6
7. Maize I. (6 years old, rancid)	18·4	128·8	18·4	110·4
8. Maize II.	16·9	118·3	19·8	118·8
9. " III. (1898)	17·2	120·4	20·0	120·0
10. Sesamé	16·0	112·0	18·1	108·6
11. Rape I.	13·7	95·9	16·5	90·0
12. Poppy (1895)	17·8	124·6	20·4	122·4
13. Linseed I. (4 years old) ...	24·8	173·6	28·2	169·2
14. " II. (Calcutta)	24·7	173·9	29·4	176·4
15. " II. (after 3 weeks)	27·6	193·2	27·9	167·4
16. " III. (oxidized)	21·5	150·5	21·7	130·2
17. " IV. (boiled 10 hours) ...	23·9	167·3	28·3	169·8
18. Tung I.	23·2	162·4	21·2	127·2
19. Castor	16·8	117·6	14·5	87·0
20. Cod-liver (old)	20·5	143·5	23·4	140·4
21. Whale (old)	14·0	98·0	15·3	91·8
22. Butter I.	8·1	56·7	5·8	34·8
23. " II.	9·4 ; 9·1	65·8	6·0	36·0
24. Mutton-fat	9·6	67·2	8·6	51·6
25. Lard	11·5	80·5	10·9 ; 10·8	65·4

It will be seen that there is a close agreement between the two calculated iodine values with the majority of these oils. With the cottonseed oil (No. 6), the rise with sulphuric acid is too high; but I know nothing of the origin of that oil, and it is quite possible that it may have been exposed to the action of light and air for some time.

It appears from the results obtained with the maize oil acids (No. 7) that exposure of the oil to atmospheric influences affects the Maumené figure of the fatty acids in the opposite direction to the iodine value. In 1895 this same specimen of oil had an iodine value (Hübl) of 122, and calculated iodine value (from the bromine rise) of 118. The calculated figure has now fallen to 115, and the oil has become rancid; so that it is not surprising that the iodine value calculated from the Maumené figure should be too high. This inference receives support from the results of Ballantyne (*Journ. Soc. Chem. Ind.*, 1891, 29), who found the ordinary Maumené figure of different oils to be considerably increased after exposure to sunlight. The results obtained with the two other specimens of maize oil show a satisfactory agreement.

Coming next to the drying oils, the Maumené iodine value of No. 13 is too high;

but here, too, the bromine thermal value shows that atmospheric oxidation has taken place. In the case of No. 14, which was a sample of Calcutta oil from Mr. Williams, the agreement is very close. No. 15 shows the effect of exposing the fatty acids of No. 14 for three weeks to atmospheric influences. No. 16 was a sample which, having been left for four years in an open bottle, had become very viscous and was covered with a thick skin. No. 17 was a sample of oil which had been boiled for ten hours. Its calculated iodine values are in close agreement, as is also the case with the sample of poppy oil (No. 12).

The specimen of tung oil (No. 18) is the same one examined by Mr. Jenkins in 1898. The sulphuric acid rise is much too great in proportion to the bromine thermal value. The iodine value calculated from the rise of temperature with bromine (127.2) agrees well with that calculated by Mr. Jenkins three years ago (ANALYST, xxiii., 118).

It is not surprising that the Maumené iodine value of castor oil fatty acids should be too high, for sulphuric acid acts differently on ricinoleic acid and oleic acid, yielding an unsaturated product in the case of the former.

The values of cod-liver oil agree well, whilst in the case of whale oil, which was a sample of unknown age, the Maumené iodine value is too high.

The results obtained with the two specimens of butter fatty acids are interesting, and it requires further research to determine whether the higher Maumené figures were due to oxyacids, or to the action of the sulphuric acid on the lower insoluble fatty acids, or to alterations in the process of manufacture. I made one experiment with palmitic acid, and only obtained a rise of 0.2° C., after deducting 0.5° C. for the rise of temperature with carbon tetrachloride. I am inclined to attribute the want of agreement in the case of the mutton fatty acids (No. 24) and lard (No. 25) to the effect of overheating during rendering, seeing that the Maumené rise is much more sensitive to the influence of external factors than the bromine thermal value.

Behaviour of Glycerides.—In the case of the oils themselves the agreement between the Maumené figure and the iodine value is, as a rule, not nearly so close as with the fatty acids, though there is still an evident proportion. The amount of heat due to the hydrolysis appears to vary in the different oils, and in some cases the strength of the sulphuric acid has a very great influence. It is possible, however, to obtain closely concordant results, and it may eventually be found possible to make a sharp distinction between the heat of hydrolysis and the heat of absorption. By the method which I have described it will also be possible for different chemists to obtain comparable results, and I would suggest that the figures obtained be calculated on the basis of an apparatus with a bromine thermal factor of 5, and that the exact strength of sulphuric acid be given.

Halogen Standard Figures.—The influence of using a different vacuum-jacketed tube and a different thermometer is shown in the following results, the acids used in each case containing 93.8 per cent. of anhydrous sulphuric acid :

II.

Oil.	Vacuum-tube I. Thermometer I. Bromine Factor = 6.		Tube II. Thermometer II. Bromine Factor = 5.52.	
	Temperature Rise with H_2SO_4 (93.8 per cent.).	Halogen Standard Figure.	Rise of Temperature.	Halogen Standard Figure.
Almond oil	° C. 12.7	15.24	° C. 13.6	14.96
Cotton oil	15.3	18.36	16.3	17.93
Oleic acid	11.7	14.04	12.5	13.75

Influence of the Duration of the Reaction.—As the rise in temperature with bromine only occupies about twenty-five seconds, whereas the rise with sulphuric acid lasts from forty-five seconds to one or even two minutes, with the weaker strengths of acid it seemed possible that a considerable error might thus be introduced if different apparatus were used and merely standardized on the bromine thermal figure.

I therefore made a number of experiments with different oils to determine the probable loss of heat.

A correction, which is rough from the physicist's point of view, but which is sufficient for ordinary purposes, can be obtained by noting the fall of temperature from the highest point attained at intervals of five minutes, and dividing the total loss of temperature by the number of minutes before the mercury ceases to fall. It becomes apparently constant at 2° or 3° above the temperature of the room, which points to the establishment of an equilibrium between any substitution which occurs and the loss of heat. The loss thus determined amounted to approximately 0.2° C. per minute with different tubes, strengths of acid, and oils. If the rise does not occupy more than a minute, this correction lies within the limit of experimental error, and may be neglected.

It is advisable, however, to use acid of more than 96 per cent. strength in order to reduce this time error as far as possible.

Influence of Different Strengths of Acid.—Archbutt (*Journ. Soc. Chem. Ind.*, 1886, 304) showed that the concentration of the sulphuric acid had a considerable influence on the rise of temperature in the ordinary method, and this is also the case with the method I have described, as is seen by the following results :

III.

RISE OF TEMPERATURE WITH ACID OF DIFFERENT STRENGTHS.

Oil.	93.8 per cent.	95.1 per cent.	96.3 per cent.	97.8 per cent.
	° C.	° C.	° C.	° C.
Oleic acid	11.8	13.25	14.6	15.7
Almond oil	12.7	14.4	16.2	18.8
Cotton oil	15.0	18.1	20.0	22.9
Linseed oil	19.6	27.5	28.1	31.2

It will be observed that the rise with 93.8 per cent. acid was disproportionately low in the case of the linseed oil.

IV.

HALOGEN STANDARD MAUMENÉ FIGURES (CALCULATED ON BROMINE THERMAL FACTOR = 5).

Oil.	H ₂ SO ₄ (93·8 per cent.).	Calculated I Value Rise × 6·35.	H ₂ SO ₄ (97·8 per cent.).	Calculated I Value Rise × 4·3.	Bromine Thermal Value.	Calculated I Value Rise × 6.
	° C.		° C.		° C.	
1. Almond ...	15·2	96·5	22·4	96·3	16·1	96·6
2. Earthnut ...	14·0	88·9	20·5	88·1	14·3	85·8
3. Olive ...	12·7	80·6	18·4	79·1	13·8	82·8
4. Cotton ...	18·3	116·2	26·6	114·4	17·5	105·0
5. Maize I. (rancid) ...	24·5	155·5	34·4	147·9	19·2	115·2
6. „ II. (old) ...	19·4	123·2	29·7	127·7	19·5	117·0
7. „ III. (1898) ...	19·2	121·9	28·6	122·9	19·4	116·4
8. Sesamé ...	18·0	114·3	25·3	108·8	17·8	106·8
9. Mustard husk ...	18·2	115·6	26·6	114·3	18·2	109·2
10. Rape I. ...	17·6	111·7	23·9	103·7	16·7	100·2
11. „ II. ...	17·0	107·9	23·2	99·7	15·0	90·0
12. „ III. (Japan) ...	15·0	95·2	22·0	94·6	16·7	100·2
13. Poppy (old) ...	25·5	161·9	38·0	163·4	21·0	126·0
14. Linseed I. (4 years old)	24·1	153·0	37·2	159·9	27·3	163·8
15. „ II. (Calcutta) ...	23·4	148·5	37·3	160·3	28·2	169·2
16. „ III. (oxidized) ...	26·0	165·1	39·9	171·5	22·2	133·2
17. „ IV. (Baltic) ...	22·3	141·6	37·2	159·9	30·2	181·2
18. „ V. (1898) ...	24·5	155·5	37·8	162·5	29·3	175·8
19. „ VI. boiled 10 hrs.	21·6	137·0	35·0	150·5	27·6	165·6
20. „ „ „ 15 „	21·7	167·7	22·3	95·9	27·4	164·4
21. „ „ „ 20 „	13·9	88·2	24·4	104·9	19·5	117·0
22. Tung I. ...	12·6	80·0	33·9	145·8	21·2	127·2
23. „ II. ...	—	—	26·2	112·6	23·7	142·2
24. Castor ...	20·8; 20·7	132·0	27·6	118·6	15·0	90·0
25. Cod-liver (old) ...	—	—	38·5	165·5	24·5	147·0
26. Whale ...	12·8	81·0	18·6	79·9	15·8	94·8
27. Butter I. ...	11·0	69·8	—	—	6·2	37·2
28. „ II. ...	10·6	67·2	—	—	5·4	32·4
29. Mutton-fat ...	9·2	58·4	—	—	8·3	49·8
30. Lard ...	11·0	69·8	16·5	70·9	10·8	64·8

If we compare these results, we see that the agreement between the different calculated iodine values is fairly satisfactory in the case of almond, earthnut, olive, maize (III.), sesamé, mustard husk, rape (I.) and Japanese rape oils.

The Maumené values of the cottonseed oil are too high, which was also the case with the fatty acids. All the specimens of rape oil were not less than three years old, whilst the poppy oil was more than six years old. This is probably the cause of the Maumené figures being too high.

The figures given by the linseed oils were invariably too low, but it is interesting that the results obtained with the 98 per cent. acid approximated more nearly to the truth. It is not improbable that complete proportion between the bromine and

Maumené figures of unoxidized oils might be obtained by the use of monohydrated sulphuric acid.

These results also confirm those given in Table III., and show that the oils are affected to a much greater extent than their fatty acids by the strength of the sulphuric acid. In the case of the boiled oils the Maumené results cannot be altogether trusted. On the addition of the acid, the entire amount of oil formed a clot round the thermometer, and it required very vigorous stirring to break up the mass, whilst even then the mercury rose but slowly.

An analogous behaviour was observed in the case of the two samples of tung oil, of which No. 1 was Mr. Jenkins's sample, and No. 2 was given me by Mr. Rowland Williams. This curious property of tung oil has already been noticed by Mr. Jenkins (*ANALYST*, 1898, xxiii., 114). The second sample was that examined by Mr. Rowland Williams (*Journ. Soc. Chem. Ind.*, 1900, 301).

The samples of cod-liver oil and whale oil were both old, and it is not surprising that the Maumené figures are too high. The results obtained with the samples of castor oil, butter, mutton-fat and lard show an excess over the bromine thermal figures, as was also noticed with their fatty acids. In certain instances the rise of temperature with the lower strength of acid was proportionately greater than with the higher strength. I am unable to offer a satisfactory explanation for this, except that the greater proportion of water in the lower strength of acid may have an influence on some secondary hydrolysis of the sulphonated product.

To summarize the foregoing results :

1. The Maumené figure determined by the method described above is in direct proportion to the bromine thermal value of the fatty acids of most unoxidized oils.
2. Castor oil, and apparently butter and animal fats rendered at a high temperature, form exceptions to this rule.
3. This relationship also applies to the glycerides, though these appear to be more influenced by atmospheric oxidation than their fatty acids.
4. The strength of the sulphuric acid has a great influence on the proportional results obtained with the glycerides, and even with 98 per cent. sulphuric acid the Maumené figures of unoxidized linseed oils are too low.
5. This modification of the Maumené test may be found useful in determining the degree of oxidation of fats and oils, inasmuch as the figure becomes greater with the decrease in the iodine value.

In conclusion, I have to express my best thanks to Mr. Rowland Williams for samples of linseed and boiled linseed oil, maize oil (II. and III.), and tung oil (II.), to Mr. Jenkins for the sample of tung oil (I.), and to Mr. Skertchly for checking the standardization of my tubes.

DISCUSSION.

Mr. JENKINS said that a weak point of the Maumené test hitherto had been that, in the case of oils like linseed and fish oils, some method of dilution was necessary to prevent foaming over, and the dilution of these oils led to results which were not easily comparable with those given by the non-diluted oils. This weak point Mr. Mitchell had met by the dilution of all oils alike. A further advantage of the

method now described was apparent when the figures were compared with some results given in a paper which he (Mr. Jenkins) had read in 1897 before the Society of Chemical Industry, when about a dozen oils were compared with regard to their Hübl values, bromine temperature reactions (calculated to iodine values) and specific temperature reactions, the latter being the results of the Maumené test compared with the rise of temperature given by water under the same conditions, the latter being taken as 100. It will be seen that in the case of such non-drying oils as neat's-foot oil and olive oil the figure for specific temperature reaction was only about 1.2 times that of the Hübl figure; but as one approached the drying oils the increase of the Hübl figure was accompanied by a much greater rate of increase in the Maumené figure, the ratio then becoming more nearly 2. One of the interesting points of the present paper was that, with this new method of applying the test, such differences of ratio largely disappeared. Possibly in the earlier methods the actual rise of temperature with the drying oils was so great as to induce secondary reactions evolving more heat, whereas in Mr. Mitchell's experiments the oils were so largely diluted with the carbon tetrachloride as to prevent this undesirable secondary rise of temperature. The author's results with tung oil were especially interesting. With the tung oil (I.), when 93.8 per cent. acid was used, the rise of temperature was 12.6°, whereas when the acid was 97.8 per cent. the rise of temperature was 33.9°. It was also peculiar, inasmuch as the iodine value calculated from the bromine thermal value was considerably lower than the iodine value calculated from the Maumené figure. On the other hand, in the case of tung oil (II.), the calculated iodine value from the sulphuric acid test was much lower than that from the bromine thermal value.

Mr. HEHNER said that, it being established that bromine was simply added on, and that the heat of bromination was simply the heat of combination of certainly two, and sometimes four, or even six, atoms of bromine, it seemed to him that the process might be regarded as, generally speaking, a uniform additive process; and seeing that in most cases the rise of temperature with sulphuric acid agreed fairly well with the bromine thermal value, it seemed as though the ordinary action of sulphuric acid upon an oily solution was simply a sulphonation process. Coming to the oxidized oils, there was something further to be considered. The oil contained an additional quantity of oxygen, which the sulphuric acid displaced, itself adding on and forming a sulphonated oil, while at the same time water was formed, which increased the rise of temperature; so that in the case of an oxidized oil the rise of temperature produced by the action of sulphuric acid was considerably increased. Similarly, there was a largely increased rise of temperature in the case of many oils which were of the nature of hydroxy compounds. The constitution of tung oil was peculiar. It had no oleic acid, or, if any, very little; but, on the other hand, it contained another unsaturated fatty acid, which crystallized in a magnificent manner, and which, he thought, probably contained three atoms of oxygen. It was quite certain that these Japanese wood oils differed considerably from one another. After all, when it was recognised that, by reason of slight oxidation or of the age of the oil, the factors were in some cases deeply influenced by the strength of the sulphuric acid employed, the analyst would naturally consider that probably he would not get

much advantage from a reaction of this kind in dealing with an oil the constitution of which might be quite unknown to him. The scientific chemist, however, would not contemplate all these reactions merely with regard to the assistance they might afford him in his business, but would probably look deeper into the question, and he (Mr. Hehner) personally felt indebted to the author for the addition to knowledge that resulted from this work.

Mr. MITCHELL said that in diluting with olive or any other oil one could never be quite sure about the oil used. Ellis had pointed out some fifteen years ago that if the rise of temperature was above 60° C. it was perfectly impossible to get concordant results, and his (Ellis's) attempts had all been directed towards keeping the rise of temperature below 60° . It might be mentioned that the use of the particular form of tube now described did not seem to be absolutely essential. He had made experiments with an ordinary boiling test-tube packed inside a beaker with asbestos wool, the bromine thermal factor of this being determined; and provided the loss of heat was not too great, or was taken into account, this arrangement answered just as well as the vacuum-jacketed tube. In the case of tung oil some difficulty was experienced owing to the clot which it formed with sulphuric acid. It was necessary to stir vigorously for four or five minutes, and even then one could not be quite sure that the full rise of temperature was obtained.

ARSENIC ESTIMATIONS RELATING TO MALT-KILNS.

By T. FAIRLEY, F.I.C.

(Read at the Meeting, April 3, 1901.)

As one result of the close attention and supervision which has lately been given to materials, etc., relating to the malting and brewing industries, the occasional presence of arsenic in malt has been established. This arsenic has been traced by a number of persons (Thomson and others) to the fuel used in kilning the malt, and in consequence, in many cases, fuel practically free from arsenic has been sought for.

Having occasion to inspect some malt-kilns, it struck me that where an impure fuel had been used for a length of time the change to an arsenic-free fuel might not give the security from contamination of the malt which would be expected.

When one considers how readily arsenical vapour is condensed on any surfaces colder than itself, the walls and floors, etc., of malting-kilns might be expected to show arsenic in the dust deposited on them where an arseniferous coke has been used. I have been greatly surprised at the comparatively large proportions of arsenic which I have found under these circumstances.

The tiles forming the floor of the malting-kiln and the walls above and below the malting-floor act as condensing surfaces for the arsenical vapours given off from impure fuel, and the arsenic appears to accumulate on them, so that the effect of the minute proportion of arsenic in the fuel may be greatly magnified.

At first this condensing action, so far as it protects the malt from contamination, may be beneficial. After a time, given walls and tiles already charged with

arsenic, it is obviously futile to change from an impure to a pure fuel so long as the tiles and surfaces through or over which the products of combustion must pass, on their way to the malt, are heavily charged with arsenic.

Some of the older tiles are unglazed and porous. In these the arsenical vapour has penetrated into the mass of the tile. Thus, in tiles weighing about 13 pounds, and measuring about 1 foot square, I have found from 109 to 36 grains of arsenic trioxide. It is evident that such tiles should be at once removed from the floor of the kiln.

Glazed tiles differ in the perfection of the glaze, according to age and manufacture. In these I have found from 25 grains of arsenic trioxide down to none—that is, when the dust adherent chiefly to the lower surface of the tiles had first been removed. In my opinion, tiles in which the arsenic has penetrated into the mass of the tile should in every case be removed.

In all cases where impure fuels have been used there cannot be too much care taken to remove all dust from tiles, floors, walls, crevices, etc., and only when this precaution is taken, and new tiles put in the floors where necessary, can the malt be protected from contamination by the change to a pure coke or fuel.

The proportion of arsenic in some of the dust adherent to the tiles is extraordinary, ranging from 1 down to 0.25 per cent. of the weight of the dust. The amount in the dust adherent to the walls is much less, from 0.06 down to 0.0025 per cent.

As the malt is only exposed for a limited time to the kilning process, the arsenic, where present in malt, is generally external, and can be removed by careful cleaning and brushing, etc., of the malt. Thus, the dust from the malt-screening machines contains arsenic frequently where none can be found in the cleaned malt. At the same time, it is sufficiently obvious that it is not right to trust to any merely mechanical process being carefully carried out perfectly, where such a dangerous substance as arsenic in a food, or article used in the preparation of food or drink, is concerned. The malt-screening process, however good in itself, was never intended to deal with such a serious problem as the removal of arsenic from the malt.

METHODS OF ANALYSIS.

The Tiles.—These were broken up and roughly pounded, then a smaller portion finely pounded and 2 to 5 grammes treated with 20 to 50 c.c. 25 per cent. sulphuric acid. In the older tiles there is calcium carbonate, and when the effervescence due to this has ceased the material is heated one to two hours on the water-bath.

Afterwards the volume of the liquid with the powder in suspension is made up to 50 or 100 c.c., and a measured portion of this put into the Marsh's apparatus. In this about 2 inches of the exit tube was heated to redness for thirty minutes. By comparison with a standard set of mirrors from known amounts of arsenic an approximate estimation of the arsenic in the tile is quickly made.

For the gravimetric estimations 10 to 20 grammes of the finely-pounded tile was treated and distilled with pure hydrochloric acid with the addition of ferrous chloride, until no more arsenic chloride came over. The arsenic precipitated as sulphide was collected, dried, and weighed. It was completely soluble in dilute ammonia.

The Dusts.—One to 5 grammes were treated with from 10 to 50 c.c. of strong sulphuric acid and about 20 c.c. nitric acid 1.42 specific gravity. When the organic matter was oxidized and the nitric acid boiled off, the liquid was allowed to cool, diluted and boiled to drive off oxides of nitrogen, and finally cooled and made up to 50 to 100 c.c. A fraction of this liquid was taken for the Marsh's test to bring the amount of arsenic within the range of the mirrors.

For the gravimetric tests 5 grammes of each dust was distilled with HCl as before, and the estimation finished as with the tiles.

I have found it difficult to obtain pure sulphuric acid capable of standing a prolonged Marsh test. For those who have similar difficulty the following method of purification may be recommended.

Many years ago I found that sulphuric acid distils quietly, like alcohol or water, in presence of alkaline bisulphates, and Maxwell Lyte and others showed that arsenic in the form of arsenic acid is not volatile with sulphuric acid.

A convenient-sized retort is about half filled with commercial "pure" sulphuric acid, to which has been added 25 to 30 per cent. of sodium or potassium bisulphate, or proportionately less sulphate. To this is added potassium permanganate or bichromate in small quantity to secure complete oxidation of any arsenic that may be present. Heat is applied by means of a gauze, rose, or ring burner, and the whole arrangement carefully screened from draughts, which, cracking the hot glass, are almost the only source of danger. About two-thirds of the acid may be distilled over.

If potassium bichromate be used, then gradually an anhydrous chromium sulphate is formed, which, settling at the bottom as a heavy powder, causes bumping, necessitating the use of a ring burner.

If this method be used to purify *ordinary* commercial acid, ammonium sulphate may be added in place of other alkaline sulphate, and acts like them. It also reacts with and destroys any oxides of nitrogen that may be present, after which the oxidizing agent may be added.

MALT-KILNS.

Percentages of Arsenic Trioxide in Tiles and Dusts.

- A. Floor tiles, unglazed: 0.12; 0.064; 0.04.
- B. „ „ glazed and cleaned: 0.03; 0.02; 0.02; 0.01; 0.008; none.
- C. „ „ dust from under surface: 1.0; 0.8; 0.75; 0.7; 0.3; 0.2.
- D. Malting-room, dust from walls above floor: 0.06; 0.04; 0.035; 0.03; 0.02.
- E. Chamber or space below malting-room, dust from walls, etc. (often chiefly culms): 0.05; 0.035; 0.03; 0.025; 0.012; 0.008; 0.007; 0.004; 0.0025. The dust giving 0.004 per cent. As_4O_6 was sifted to separate culms, and the fine dust then gave 0.07.
- F. Malt-screening machines, dust containing much organic matter: 0.01; 0.004; 0.0016.

Some of the above estimations were repeated gravimetrically, with the results

					Gravimetric Test.		Mirror Test.
					As ₄ S ₈ Grammes.	As ₄ O ₆ %	As ₄ O ₆ %
A. Tiles	...	...	10	grammes gave	0.0128	0.10	0.12
"	...	...	20	" "	0.0179	0.072	0.064
C. Dusts	...	...	5	" "	0.0659	1.06	1.00
"	...	...	5	" "	0.0465	0.74	0.80
"	...	...	5	" "	0.0464	0.74	0.75
"	...	...	5	" "	0.0410	0.66	0.70

I hope these results may prove useful to maltsters and others interested in helping them to avoid a possible source of danger—even where a pure fuel is now adopted.

Mr. A. B. Shepherd, B.Sc., has assisted me in the analytical work in this paper, and I have pleasure in stating that my best thanks are given to him.

DISCUSSION.

Mr. BAKER said that he had recently examined several samples of dust collected from malt-houses of the more modern type, in which the heated air was diffused by means of a "baffle plate" fixed above the fire and underneath the malting-floor. The fuel used would be coke, or a mixture of anthracite and coke, or if coal only were used the kilning operation would in some cases be concluded with a small quantity of foundry coke to "finish off the goods." The average quantity of arsenic present in the dust from different parts of the kiln was about $\frac{1}{3}$ of a grain per pound. The dust which collected underneath the baffle plate seemed to be very rich indeed in arsenic, containing from $1\frac{1}{2}$ to 2 grains per pound. On the top of the baffle plate a large quantity of malt coombs and dust collected, and these were comparatively poor in arsenic. When the malt came off the floor it was subjected to a process of screening. In the case of malt of very good quality containing in the finished state not more than $\frac{1}{500}$ grain of arsenic per pound, the coombs from the last screen would contain as much as $\frac{1}{33}$ grain of arsenic per pound. With regard to the question of whether brushing would remove arsenic from malt, he thought that when a large quantity of arsenic was present possibly a portion of it might be removed in this way, but that when the quantity of arsenic was small—say $\frac{1}{300}$ or $\frac{1}{400}$ grain per pound—it made absolutely no difference whether the malt was brushed or simply cleaned in the ordinary way.

Mr. FAIRLEY said that the older kilns consisted, as it were, of one room on the top of another, the upper room having the malting-floor, while the lower, which had very thick walls, contained the fireplaces, the products of combustion passing upwards through tunnels in the side walls. The sample of dust that contained 1 per cent. of arsenic was from one of the modern arrangements, while that which contained 0.8 per cent. was from an old-fashioned kiln.

THE GUTZEIT TEST FOR ARSENIC.

BY F. C. J. BIRD.

(Read at the Meeting, April 3, 1901.)

THE Gutzeit method of detecting arsenic, like that of Marsh, depends primarily on the formation of arsine by the action of nascent hydrogen generated from zinc and hydrochloric or sulphuric acid in contact with the arsenic-containing substance. Originally the arsine was allowed to act on either nitrate of silver or mercuric chloride paper; but so many objections apply to the use of the former, that latterly the term "Gutzeit's test" has come to be associated with the employment of mercuric paper only, on which arseniuretted hydrogen produces a yellow stain. The convenience and simplicity of this test would doubtless cause it to be far more generally employed were it not for the occasionally uncertain and misleading nature of its indications.

The chief objections to the method, as ordinarily carried out, may be summarized as follows :

1. It is not absolutely negative. Traces of arsenic associated with such substances as certain coal-tar colours, compounds reducible by nascent hydrogen, soaps, etc., or existing as arsenates in very small proportion, may escape detection.

2. Unless the state of oxidation of the arsenical compound is known, it fails as an approximately quantitative method; for any attempt to deduce the amount of arsenic present from the depth of the stain is likely to result in error, on account of the fact that arsenates yield a much paler stain in a given time than arsenites. The intensity of the stain is also influenced by the degree of humidity of the mercuric chloride paper. Water, especially when warm, dissolves the stain completely, leaving the paper white; dampness and extreme dryness of the mercuric chloride paper are alike prejudicial to the production of a stain of correct intensity.

3. Stains which either resemble or may mask or deepen a true arsenical stain are produced by the hydrides of phosphorus, sulphur, and antimony. Sulphuretted hydrogen (and also selenium hydride) can be absorbed by lead acetate solution; but phosphoretted hydrogen, always a possible impurity, passes through the liquid, and tints the mercuric chloride paper full yellow. Acid cuprous chloride solution was tried as an absorbing agent for this interfering compound, but proved unsatisfactory. Antimoniuretted hydrogen gives a yellowish-brown to full brown and black coloration, which gradually fades on exposure to air. When dealing with colourless inorganic salts, such as phosphate of soda, etc., oxidation by iodine, bromine, or permanganate is an effective safeguard against both phosphine and hydric sulphide; but with some organic substances either the halogen is absorbed, or the permanganate reduced almost indefinitely; and as with an excess of either oxidizing agent the presence of arsenic may be completely masked, preliminary oxidation has but a limited application.

4. No simple method has hitherto been described either of distinguishing between arsenical and interfering stains, or of demonstrating the real nature of a supposed arsenical stain.

From the foregoing considerations it is evident that the Gutzeit test in its present form is at best but a preliminary test, not admitting of even approximately accurate quantitative deductions (excepting in a few special instances), and occasionally liable to mislead on account of the uncertainty of the absence of phosphoretted compounds (especially in coloured substances), or of traces of sulphuretted hydrogen unabsorbed by the lead acetate during a sudden rush of gas. On the other hand, if the difficulties mentioned could be satisfactorily overcome, the test itself offers several obvious advantages.

If uniform results are to be always obtained with tests like those of Marsh and Gutzeit, it is essential that the evolution of arsine take place under fixed and constant conditions. The rate of formation of arsine appears to be regulated, firstly, by the concentration of the arsenical solution, and, secondly, by the energy of the reaction between the zinc and acid, this latter being dependent on the strength of the diluted acid, and especially on the temperature of the liquid. It can be easily demonstrated that in similar solutions 100 square centimetres of mercuric chloride paper are coloured to a full yellow by 1 milligramme As_4O_6 by the Gutzeit reaction in a few minutes, whilst the same effect is not produced on 1 square centimetre by $\frac{1}{100}$ milligramme As_4O_6 in less than ten minutes or more, all other conditions being precisely equal. So also in the Marsh-Berzelius test, when the time limit is half an hour, it is generally noticed that the greater part of the arsenic is deposited during the second fifteen minutes, when the liquid in the generating flask has become warm and the chemical action energetic. Uniformity of conditions would therefore appear to be best insured by: (a) The complete solution of a given weight of zinc in a given time; (b) the maintenance of a constant temperature in the generating flask; and (c) the limitation of the volume of the solution in the generating flask to a given quantity. I have accordingly taken 4 grammes of zinc, completely dissolved in fifteen minutes at the boiling temperature of a liquid measuring not more than 100 c.c., as the basis of a satisfactory method of conducting the Gutzeit test, and have found the same principle of reaction at a boiling temperature to apply equally well to the Marsh-Berzelius method.

The apparatus employed for this modification consists of a flat-bottomed 150 c.c. flask, furnished with a small upright reflux condenser and a 10-inch thistle funnel, above which is supported a tap-separator for the regular supply of acid to the flask. The exit tube of the condenser is curved over, and passes into a small wash-bottle containing 10 per cent. lead acetate solution, whence a suitable tube carries the gas to the mercuric chloride paper disc. Four grammes of arsenic-free zinc in very small fragments are placed in the flask, together with the suspected substance, dissolved in 30 c.c. water. The solution is heated to the boiling-point on a hot-plate, and kept at that temperature by a small flame underneath; 15 c.c. of pure hydrochloric are then gradually run in by the tap-funnel, a steady evolution of gas being maintained by adjusting the stopcock, so that the acid is supplied in a regular succession of drops. The rate of flow should be such that the whole of the acid is delivered in ten minutes; the contents of the flask are then boiled for five minutes longer, when the zinc will have disappeared and the test may be considered completed. The quantity of acid used is in all cases half the volume of the liquid in the flask. Seventy c.c. of beer, for

example, require 35 c.c. of acid, all of which should be run in during the ten minutes. Whenever possible, it is convenient to keep the volume of the solution within 30 c.c. ; but with original weakly arsenical liquids, as beer, the limit can be extended to 70 c.c. without disadvantage.

A similar arrangement with the zinc, etc., proportionately increased if necessary, suffices for the adaptation of the same principle to the Marsh-Berzelius method. Lead acetate solution is more effective in keeping back sulphuretted hydrogen than the roll of dry lead paper often recommended in analytical treatises. Traces, even, of sulphuretted hydrogen have a decided influence on the appearance of the Marsh-Berzelius mirror, and to the presence of small quantities of this gas in the mixture of hydrogen and arsine, which have escaped fixation by the lead paper roll, I am inclined to attribute the greater sensitiveness of hydrochloric acid as compared with sulphuric acid when used in the Marsh-Berzelius apparatus. The purest analytical sulphuric acid diluted and allowed to act on pure zinc almost invariably yields a gas which quickly blackens moist lead paper ; hydrochloric acid similarly treated usually gives but a faint reaction. A comparison of the effect of the two acids with known quantities of arsenic, the sulphuretted hydrogen having been completely removed by lead acetate *solution*, has shown no perceptible difference in the resulting mirrors. Hydrochloric acid is, however, the more convenient for the reasons given by Mr. Otto Hehner some weeks ago when describing his admirable method of applying the Marsh-Berzelius process to the quantitative determination of minute traces of arsenic.

The powerful reducing action of nascent hydrogen evolved at the boiling temperature of the liquid in this modified Gutzeit test renders possible the detection of traces of arsenic in certain combinations which in the cold are liable to be missed. Under these conditions the stain from an arsenate is practically identical with that from its equivalent of arsenite ; even $\frac{1}{100}$ milligramme as arsenate makes its presence evident within two or three minutes. The time requisite for an experiment is reduced to fifteen minutes, and neither sulphurous acid nor substances themselves reducible by nascent hydrogen interfere with the formation of arsine. Even dry precipitated sulphide of arsenic ($\frac{1}{50}$ milligramme) readily yields its arsenic at the boiling temperature if the solution contain water and acid only ; much glucose, however, interferes with or entirely prevents reaction.

Beer and similar liquids require no preliminary treatment. Frothing, often so troublesome with beer samples, does not occur at a boiling temperature, the volatilization and condensation of the alcohol on the surface of the liquid effectually breaking up the froth as it forms ; 2.5 to 5.0 c.c. of alcohol added to the liquid in the generating flask acts in a similar manner with substances containing dextrin, etc., which from the same cause are often equally difficult to deal with.

The limit of sensitiveness of the Gutzeit test has been variously stated. One-hundredth milligramme As_4O_6 (or considerably less of arsenic acid) is a figure which has been given quite recently, whilst in the ANALYST for 1891 Curtmann states that $\frac{1}{10000}$ milligramme in 1 c.c. produces a yellow stain in thirty minutes, and that $\frac{1}{100000}$ milligramme gives a barely perceptible stain after one hour. My own experience points to $\frac{1}{250}$ milligramme of an arsenate and $\frac{1}{50}$ milligramme As_4O_6 as about the smallest amounts capable of producing a distinctly recognisable stain with

a time limit of half to one hour in the ordinary way of applying the test. Just, however, as the sensitiveness of the Marsh-Berzelius method can be enormously increased by contracting the diameter of the heated tube, so also by decreasing the area of the mercuric chloride disc does the Gutzeit test gain in delicacy. The limit of sensitiveness of the modified method with a 5 millimetre disc appears to be $\frac{1}{100}$ milligramme As_4O_6 ; whether existing as arsenate, sulphide in an aqueous liquid, or mixed with sulphurous acid, soap, reducible coal tar compounds, etc., is immaterial. This quantity of arsenic, reacting at a boiling temperature, stains a 5-millimetre mercuric chloride paper disc to full intensity in about ten minutes, and the stain is capable of being identified without difficulty by two reactions to be subsequently described. Stains are obtainable with much smaller amounts of arsenic (perhaps $\frac{1}{1000}$ milligramme), but such stains do not admit of satisfactory confirmation.

A small piece of apparatus useful for the concentration of the arsenical stain consists of a short piece of wide glass tube contracted at one end to a diameter of 5 millimetres, the contracted extremity being ground flat. A disc of mercuric paper (filter-paper saturated with 5 per cent. mercuric chloride solution, dried, folded, and cut into circles with a suitable cork borer) is attached to the ground extremity of the tube previously smeared with thick mucilage. A second similar tube bearing a paper disc is placed over the first, the joint being either a ground one or extemporized with rubber tubing, and the whole is surmounted by a third tube, the extremity of which is drawn out and curved over in order to prevent the gas from escaping too freely. The first or lower tube, drawn out below to a smaller diameter, communicates with the lead acetate wash-bottle or bulb previously mentioned. By this arrangement the hydrogen mixed with arsine passes through the pores of the mercuric paper under some pressure and thorough deposition of the arsenic is ensured; the pressure existing in the apparatus is usually represented by 6 or 7 inches of liquid in the funnel tube.

The absence of any means of demonstrating the true nature of the Gutzeit stain has long been recognised as the most fatal objection to the test. In order to remove this defect if possible, I have investigated the action of various reagents, and have found that treatment of the stain with boiling hydrochloric acid affords a ready means of identification, and that its arsenical nature can be subsequently confirmed by a special application of Bettendorff's stannous chloride reaction.

On submitting the stains produced by SH_2 , PH_3 , and AsH_3 to the action of water alone, the following effects are observed: The sulphuretted stain is hardly affected by cold, but is almost entirely dissolved by hot water. The stain due to phosphoretted hydrogen becomes of a paler but brighter lemon yellow with either hot or cold water, whilst water even but slightly warm washes out both the mercury and arsenic compounds from the arsenical stain, leaving the paper colourless. The subjoined table exhibits the marked distinction drawn by hot strong hydrochloric acid between stains on mercuric paper due to sulphuretted hydrogen, phosphoretted hydrogen, anti-moniuretted hydrogen and arseniuretted hydrogen:

	Appearance of Stain.	STRONG HYDROCHLORIC ACID.	
		Cold.	Boiling.
SH_2 .	Yellow to dull brown.	Stain dissolves slowly.	Stain dissolves immediately, leaving paper colourless.
PH_3 .	Yellow.	Bright lemon-yellow.	Somewhat intensified; bright lemon-yellow.
SbH_3 .	Brown-yellow to blackish-brown; fades on exposure to air.	Stain dissolves slowly.	Dissolves immediately; paper retains a gray tint.
AsH_3 .	Yellow to orange and orange-brown.	Stain intensified; full lemon-yellow to orange.	Stain further intensified; brick-red to deep red-brown.

In the practical application of the above reactions, the stained discs of mercuric chloride paper are detached from the tubes by touching the edges of the discs with a moistened glass rod. They are placed in a watch-glass, about 1 c.c. of pure HCl (free from Cl) added, and the whole heated over a flame protected by an asbestos sheet until the acid boils. The liquid is then poured off and rejected, and the operation repeated. With $\frac{1}{100}$ milligramme of arsenic, the first disc will now be brick-red, and the second a faint orange. The treatment with HCl removes the salt of mercury, which would otherwise render the stannous chloride confirmation less distinct. The discs are now warmed with $\frac{1}{2}$ c.c. HCl, and the arsenical compound dissolved by the addition of one or more drops of bromine-hydrochloric acid, avoiding any large excess. The pale yellow liquid is poured off into a small test-tube 3 inches $\times$ $\frac{1}{4}$ inch, any residual acid displaced with one or two more drops of HCl, an equal volume of 30 per cent. stannous chloride solution in HCl added, and the contents of the test-tube warmed, when, if $\frac{1}{100}$ milligramme arsenic be present, the characteristic pink-brown coloration of Bettendorff's reaction makes its appearance almost immediately. With $\frac{1}{100}$ milligramme these reactions are very definite, and the depth of tint for that quantity, both with boiling hydrochloric acid and subsequently with stannous chloride, becomes easily recognisable. Phosphorus, sulphur, and antimony stains, when similarly treated, give negative results. The bromine-hydrochloric acid is strong hydrochloric acid containing sufficient bromine to impart a deep yellow colour. The stannous chloride reagent is prepared by dissolving 30 grammes of crystallized stannous chloride in 150 c.c. of pure hydrochloric acid and boiling down with a few fragments of metallic tin to 100 c.c. It should remain perfectly colourless when heated with an equal volume of hydrochloric acid and allowed to stand for some time.

The brick-red to deep red-brown colour produced by boiling HCl is very characteristic. Even in a mixed stain from $\frac{1}{100}$ milligramme As_4O_6 with hypophosphite and much sulphite (the SH_2 being purposely unabsorbed), the reddish tint due

to arsenic is distinctly perceptible, and the stannous chloride reaction obtainable without difficulty.

Imperfect removal of mercury salt from an arsenical stain does not seriously interfere with the stannous chloride reaction, although it is preferable to obtain a solution as free from mercury as possible. When a solution containing mercuric chloride only is treated with stannous chloride, a precipitate, chiefly calomel, is produced, which on subsidence leaves the supernatant liquid perfectly colourless. In the presence, however, of $\frac{1}{100}$ milligramme of arsenic in 1 c.c. volume, the liquid, when it becomes clear, is seen to have a distinctly perceptible pink-brown tint.

For ordinary qualitative detection of arsenic, the apparatus employed should include some arrangement for washing the gas through lead acetate solution, and the nature of the stain produced should be determined as described. The simple and ingenious apparatus devised by Mr. C. T. Tyrer, fulfils these conditions admirably, and its positive indications, confirmed by HCl and SnCl_2 , may in all cases be relied upon. I think, however, it is possible to go further, and not only make the Gutzeit test conducted at a boiling temperature a true negative test (with some slight reservation, such as when sulphide of arsenic is associated with certain organic substances, etc.), but also to extend its principle to the approximate quantitative determination, in the following sense, of traces of arsenic.

A convenient and easily recognisable standard of comparison is afforded by $\frac{1}{100}$ milligramme As_4O_6 . By taking an amount of the substance under examination corresponding to any standard limit of arsenical impurity agreed upon for that substance (such limits, it is to be hoped, will be decided upon in the near future for all the more important chemicals, food products, etc.), it appears possible to say, with the minimum of expenditure of time and trouble, whether the limit has been exceeded or not. In this way, with a limit of $\frac{1}{100}$ grain per gallon (*e.g.*, beer), the miniature gallon of 70 c.c. would be taken for the test = 1 part in 7 millions. With 10 grammes of material $\frac{1}{100}$ milligramme arsenic = 1 part in 1 million, with 7 grammes $\frac{1}{100}$ grain per pound, with 1 gramme 1 part in 100,000, etc. I think the Gutzeit test, for rapid approximately quantitative determinations, such as the foregoing, has very considerable possibilities.

The apparatus figured opposite has been devised with the view of combining in a single piece the condenser, wash-bottle, 5-millimetre tubes, etc. It is constructed entirely of glass, with ground joints as shown, and admits of rapid and effective cleansing by rinsing each part with a stream of water from the laboratory tap.

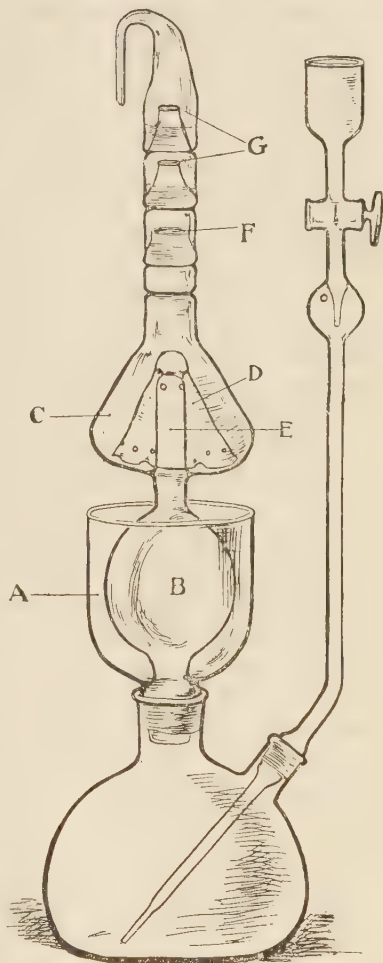
The sketch is almost self-explanatory. The tap-funnel shown on the right-hand side is for delivering the acid slowly into the flask; the glass cup above the flask is filled with water, taking the place of a condenser, and the next bulb contains 10 per cent. lead acetate solution. The flow of acid into the gently-boiling liquid should be adjusted by the stopcock to a regular succession of drops, in order to maintain a uniform evolution of gas and a slight pressure in the apparatus equal to a column of liquid 5 or 6 inches high in the vertical delivery-tube. With this apparatus a third tube is provided, bearing a disc of mercuric paper 20 mm. in diameter, for use when the quantity of arsenic is considerable, as indicated by the immediate staining of the lowest disc.

Marsh's test has been shown by Mr. Otto Hohner to be sensitive to $\frac{1}{1000}$ of a milligramme of arsenic; with Gutzeit's the limit (capable of confirmation) is reached at $\frac{1}{100}$. This modified method has only been applied to the detection of arsenic in chemical products, syrup, glucose, beer, etc.; and to these classes of substances alone are the foregoing statements intended to apply.

I have ventured to bring these results before the members of this Society, as my own experience with the modifications described has been so favourable that I felt they were, at all events, worthy of trial by others. Without any regard to the admitted facility of application of the Gutzeit test, it appears to me to be a distinct advantage to have at one's disposal an alternative and approximately quantitative method which will, with a moderate quantity of material, rapidly indicate whether the arsenical impurity of a given substance be near or far removed from the limit agreed upon for that particular substance. I also trust that the use of the hydrochloric acid and stannous chloride identification reactions will prevent the recurrence of those apparently inexplicable discrepancies between the results of the Marsh-Berzelius and Gutzeit methods which have been a not uncommon experience in the past.

DISCUSSION.

Mr. CHARLES T. TYRER thought that in Mr. Bird's paper rather too much stress had been laid upon the quantitative side of the Gutzeit test. The value of the test for qualitative purposes, however, when used with the addition of a lead acetate bulb, had been recently demonstrated by Mr. William Thomson. He was afraid he could not appreciate the advantage of carrying out either Gutzeit's or Marsh's test at boiling temperature. It seemed to him that it would be quite impossible to obtain concordant results, for an increase or decrease in the rate of heating must surely give rise to discrepancies. The rate of evolution of the gas could certainly be controlled better in the cold than at a high temperature. When a statement as to the quantity of arsenic present had to be made, on the basis of a stain, or of an unweighable deposit or mirror, it seemed to him that such statement ought only to be made with



A, Cup containing water; B, watch-shaped bulb, acting as condenser for aqueous vapour; D, E, inverted funnel, for washing the gas through lead acetate solution in C; F, lead acetate paper disc; G, 5 mm. mercuric chloride paper discs, fastened gas-tight at their edges to the contracted extremities of the glass-tubes at G.

the qualification "approximately." The necessity of relying upon a stain or mirror, the intensity of which might vary according to the conditions and the duration of the operation, was unfortunate; but where, in determining minute quantities of arsenic, a stain had to be relied upon, a method recently described by Dr. Albert Atterburg, of Kalmar, Sweden (*Chem. Zeitung*, vol. xxv., No. 25, p. 264) seemed capable of becoming a successful rival of the present quantitative methods. The process depended on the fact that arsenious acid, when heated with concentrated hydrochloric acid, was easily volatilized, the arsenious chloride vapour being readily condensed quantitatively into water. This solution was treated with nitric acid and evaporated to dryness, when all the arsenic was left in the residue. On treating the residue with a hydrochloric acid solution of sodium hypophosphite, and again evaporating to dryness, the arsenic was deposited on the bottom of the basin in the form of one or more rings of a colour varying from gray to black, the quantity being determined by means of a comparison experiment made simultaneously with a known quantity of arsenic. The process was capable of determining with approximate accuracy quantities of arsenic as small as 0.01 milligramme.

Mr. BIRD said that the difficulty suggested by Mr. Tyrer of maintaining a constant evolution of gas at boiling temperature did not really occur in the process as the acid was added in regulated drops, and the gas generated under a certain pressure, so that it was obliged to force a passage through the substance of paper. The flow of acid was so adjusted that a column of liquid about 4 to 6 inches high was constantly maintained in the delivery tube. He had not meant to infer that the sulphuric acid itself contained sulphuretted hydrogen. What he meant was that with the best samples of sulphuric acid the gas evolved discoloured lead paper very quickly, which he did not find to be the case with hydrochloric acid. His contention was that sometimes dry lead acetate paper did not keep back the sulphuretted hydrogen completely, and then a trace came over and modified the appearance of the mirror in the Marsh-Berzelius tube.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOODS AND DRUGS ANALYSIS.

The Composition of Coffee from the Grand Comoro Island. G. Bertrand. (*Bull. Soc. Chim.*, 1901, xxv., 379-381.)—The coffee plant discovered by Humblot is indigenous to this island. It was at first regarded as a distinct species, and named provisionally by Baillon *C. Humblotiana*. Froehner, however, does not admit this, and regards it as merely a variety of *C. Arabica*.

It is distinguished by the remarkable fact that it contains no caffeine, the author obtaining no trace of that alkaloid on extracting 1 kilogramme of the powdered berries. He is therefore inclined to agree with Baillon in regarding this coffee-plant as a separate species. As evidence that the climate and soil of Grand Comoro have

not influenced the composition of the plant, he gives the following analyses of the berries of *C. Humblotiana* and of *C. Arabica* which had been grown in the island :

	<i>Coffea</i> <i>Humblotiana</i> , Per Cent.	<i>Coffea</i> <i>Arabica</i> , Per Cent.
Water	11.64	9.74
Ethereal extract	10.68	5.76
Alcoholic extract	8.42	12.10
Reducing sugars	0.80	0.29
Non-reducing sugars	4.20	4.86
Total nitrogen	1.50	1.95
Ash	2.80	3.66
Caffeine	0.00	1.31

C. A. M.

Determination of Scammony for Commercial Purposes. P. L. Aslanoglou. (*Chem. News*, vol. lxxxiii., p. 146.)—A weighed quantity of scammony is extracted by warming with ether, several times in succession, each extract being filtered through cotton-wool. After washing the filter with warm ether the filtrate is treated with turpentine and left to stand for some hours, whereupon scammony, being insoluble in turpentine, comes down as an oily precipitate, leaving any accompanying gum-resins behind in solution. The precipitate is washed with turpentine, evaporated gently on the water-bath, and weighed. The insoluble earthy matter is estimated by drying the filter and contents, followed by incineration and weighing, the filter ash being deducted. The foreign gum-resins are found by evaporating the ether-turpentine solution.

C. S.

[This method seems to present some difficulties.—W. C.]

ORGANIC ANALYSIS.

Preparation of Chemically Pure Oxalic Acid. O. Schmatolla. (*Apoth. Zeit.*, 1901, xvi., 194; through *Chem. Zeit. Rep.*, 1901, 95.)—Fifty grammes of commercial oxalic acid are dissolved in 100 grammes of absolute alcohol on the water-bath, and the solution is allowed to cool and settle. It is filtered, shaken with 2 or 3 drops of 1:2 sulphuric acid, put aside overnight, decanted from any deposit of sulphates, the spirit distilled off, the residue dissolved in 200 or 300 c.c. of water, and the liquid left for several hours in the cold. Any impurities separating as a heavy oil are removed, the solution is filtered, allowed to crystallize, the crystals being finally dried at 35° or 40° C., and then over calcium chloride in a desiccator.

F. H. L.

On the Breinl Reaction for the Detection of Sesamé Oil. A. J. J. Vandevelde. (*Bull. de l'Ass. belge.*, 1900, xiv., 222-226.)—In Breinl's reaction a 3 per cent. alcoholic solution of the aromatic aldehydes *p*-oxybenzaldehyde, vanillin, piperonal or heliotropin is used instead of furfural. One c.c. of the reagent is added to 10 c.c. of the oil, and the mixture shaken with 10 c.c. of concentrated hydrochloric acid, a violet coloration being obtained in the presence of sesamé oil.

The author finds that olive, clove, linseed, almond, arachis, poppy, colza, castor and neatsfoot oil give slight colorations in this test, whilst a very pronounced colour is given by liver and rosin oils.

Comparative experiments have also shown that the Badouin reaction is more pronounced and lasting than Breinl's reaction. Breinl proposed to use a petroleum spirit solution of sesamé oil, but the author states that petroleum spirit and hydrochloric acid give violet colorations with vanillin and piperonal by themselves.

The higher the boiling-point of the petroleum spirit the more pronounced is the reaction, and an intense reddish-violet colour is obtained with petroleum spirit boiling at 130° C. Moreover, vanillin hydrochloride and piperonal hydrochloride have strong dyeing properties, and wool immersed in a solution of them is dyed violet. The colour cannot be extracted with any of the ordinary solvents. On treatment with ammonia it changes to red.

C. A. M.

The Purification of Phloroglucinol. G. S. Fraps. (*Amer. Chem. Journ.*, xxiv., 270.)—In the determination of pentosans by distillation with hydrochloric acid, the phloroglucinol used for precipitating the furfural must be free from diresorcinol. By the following method a product is obtained giving results agreeing well with those given by Merck's phloroglucinol, which is very expensive: 11 grammes phloroglucinol are gradually added, with constant stirring, to 300 c.c. hot hydrochloric acid specific gravity 1.06. The hot solution is then poured into enough of the same hydrochloric acid to make the volume up to 1,500 c.c., and the difficultly soluble diresorcinol allowed to crystallize out. The solution is filtered immediately before use.

A. G. L.

The Essential Oil of Kuskus Grass. E. Theulier. (*Bull. Soc. Chim.*, 1901, xxv., 454-465.)—This oil is obtained from the roots of *Andropogon muricatus*, which is popularly known as *Kuskus*, or Indian dog-grass. The oil extracted in India is usually obtained by distilling a mixture of the grass and Santal-wood, and but little of the pure product is exported.

The chief source of the oil sent to Europe is the Isle of Réunion. The yield from the dried roots usually varies from 0.1 to 0.8 per cent., though in exceptional cases it may be as much as 3 per cent.

The author has examined two specimens of the oil, the first of which he extracted himself, whilst the second was a sample of Bourbon oil. These gave the following results:

	I.	II.
Specific gravity at 20° C. ...	1.0091	0.986
Optical rotation at 20° C. ...	+ 35°10'	+ 28°
Solubility in 80 per cent. alcohol ...	1 in 1.5	1 in 1.5
Total saponification value ...	44.40	18.28
Saponification value of esters ...	11.90	12.12
Acid value ...	32.48	6.16

On distillation under reduced pressure (25 millimetres) the following fractions were obtained from 200 grammes of the oils :

Fractions.		Specific Gravity.	Rotation at 20° C.	Solubility in Alcohol, 80 per cent.	Total Sap. Value.	Sap. Value of Esters.	Acid Value.
C°.	Grammes.						
I. (a) 146—155	15·50	< 1	− 3°10′	Insol.	22·4	4·2	18·2
(b) 155—170	35·80	At 21° C. = 0·9735	+ 2°18′	„	14·0	7·0	7·0
(c) 170—185	50·15	At 20° C. = 1·0055	+ 19°54′	1 in 2	22·4	14·0	8·4
(d) 185—205	34·10	At 21° C. = 1·0201	+ 36°20′	1 in 1·5	56·0	42·0	14·0
(e) 205—210	15·20	—	+ 34°8′	1 in 1	98·0	75·6	22·4
(f) Residue	19·25						
II. (a) 144—154	30·10	At 19° C. = 0·9515	At 21° C. − 5°50′	Insol.	16·8	2·8	14·0
(b) 154—167	67·50	0·9683	+ 0°22′	„	5·4	1·6	3·8
(c) 167—177	60·60	At 21° C. = 0·9992	+ 31°30′	1 in 1	14·0	4·2	9·8
(d) 177—185	30·80	At 22° C. = 1·0001	+ 51°12′	„	25·2	9·8	15·4
(e) Residue	11·00						

C. A. M.

Examination of Commercial Diastase for Liquefying Power. G. Barth. (*Zeits. angew. Chem.*, 1901, xiv., 368.)—This article contains an account of the methods adopted for, and the results obtained on, examining eight different samples of German and French diastase. The diastatic power was determined by the Lintner process (*cf.* ANALYST, 1896, xxi., 124), and the liquefying power was estimated by the following method, also due to Lintner: Ten grammes of air-dried potato starch are mixed with 100 c.c. of water, and kept as a uniform cream by repeated agitation. With the aid of a wide-ended pipette, 10 c.c. of the cream are measured out into each of a series of ten test-tubes, and to the tubes are added increasing quantities (from 0·1 to 1·0 c.c.) of the diastase solution. They are next placed in a water-bath at 70° C., shaking constantly before and during gelatinization. When the contents have become solid, the tubes are put into another water-bath maintained at the temperature at which liquefaction is to be observed, and they are finally examined visually at intervals of ten minutes. In this manner the products may be divided into six classes according to their appearance: (1) The mass will not move on inverting the tube; (2) it moves with difficulty; (3) it moves easily; (4) it yields large bubbles on shaking; (5) it yields a persistent froth; and (6) the liquid becomes clear and deposits starch-cellulose.

The effect of the various preparations upon 10 per cent. starch-paste was also examined. Thirty grammes of starch were mixed with 280 c.c. of cold water and 10 c.c. of a liquid containing 0·25 gramme of diastase. This was agitated, and raised to 70° C. for liquefaction. After cooling to 62°, another 10 c.c. of diastase solution was added, and the whole was kept stirred between 60° and 62°, until iodine showed that all starch had disappeared. The liquid was filtered, and the dry substance and the specific rotatory power at 17·5° determined. The reducing power of the samples

was ascertained by carrying out Wein's maltose estimation. Dextrose in the products of reaction was tested for by heating 20 c.c. of the 10 per cent. solution with 2 grammes of phenylhydrazine and 2.2 grammes of 5 per cent. acetic acid on the water-bath for seventy-five minutes, dextrosazone then separating as fine yellow needles.

The results are given in the annexed table. It will be seen that there is no connection between the diastatic and the liquefying power of the materials.

	Taka.	Witte.	Merck.	Remy.	Defresne.	Jeune.	Billault.	Chaix.
Water	10.35	10.47	7.75	11.64	10.21	5.17		
Dry substance ...	89.65	89.53	92.25	88.36	89.79	94.83		
Ash	33.51	5.64	17.37	2.11	7.30	1.49		
Nitrogen, Kjeldahl	2.65	13.09	6.77	0.84	5.05	1.02	0.83	0.31
Proteid, N $\times$ 6.25	16.56	81.81	42.31	5.25	31.56	6.38	5.19	1.93
Diastatic value	8.63	27.4	11.5	—	Very small	Very small		
Diastase used per 100 c.c. ...	0.255	0.0832	0.1737	—	0.204	0.5088		
Specific rotatory power	146.7	156.1	151.7					
Dextrose produced	Much	None	None					
Iodine reaction of diastase solutions	None	Very faint	Very faint	Blue colour	Blue colour	Red colour	Blue colour	Blue colour
Liquefying power at 65° C. ...	Strong	Strong	Very strong					
Diastase used per 100 c.c. ...	0.20	0.20	0.1993					

F. H. L.

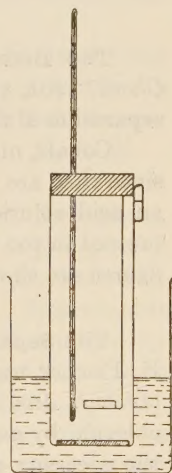
Determination of Urea in Urine. A. Braunstein. (*Zeits. physiol. Chem.*, 1900, xxxi., 381; through *Chem. Zeit. Rep.*, 1901, 62.)—The author finds that the Mörner-Sjöqvist method of estimating urea is useless when applied to liquids containing hippuric acid, Bödtker's statement to the contrary notwithstanding. He gives the following process, which is simple and accurate: 5 c.c. of urine are treated with 5 c.c. of a mixture of barium chloride and hydroxide, and 100 c.c. of alcohol-ether (2 : 1) are added. After standing all night in a closed flask, the liquid is filtered, the precipitate washed six or seven times with 50 c.c. of the alcohol-ether, and the filtrate evaporated at a temperature not exceeding 55° C. When the solvents have disappeared, a little water and a pinch of magnesium oxide are introduced, and the whole is again evaporated till the vapours are no longer alkaline. The residual liquid (10 or 15 c.c.) is run into a small Erlenmeyer flask, in which 10 grammes of crystalline phosphoric acid have been placed, and heated in an air-bath for four and a half hours at a constant temperature of 140° to 145° C. When cold, the mass is taken up in water, brought into a Kjeldahl flask, made alkaline with potassium hydroxide, and the ammonia distilled into standard sulphuric acid. The liquid does not become warm when made alkaline, so there is no fear of losing ammonia.

F. H. L.

The Estimation of Hippuric Acid. W. A. Cates. (*Chem. News*, vol. lxxxiii., p. 121.)—The latter part of the Bunge and Schmiedeberg method may be shortened by taking up with hot water the residue from the petroleum ether extraction, and titrating direct with decinormal caustic soda, in presence of phenolphthalein. The end point is very satisfactory, although urinary pigment is present; and the results agree well with those of the gravimetric method. C. S.

A Comparative Method for Determining the Fusing-points of Asphalts. Charles F. Mabery and Otto J. Sieplein. (*Journ. Amer. Chem. Soc.*, xxiii., 16.)—Since the fusing-points of asphalts vary with the conditions of heating, the following standard method, which yields good comparative results, is proposed by the authors: In a glycerin bath a moderate-sized beaker is placed containing a narrow beaker closed with a cork carrying a thermometer. Through the cork is also inserted a strip of metal, $\frac{1}{2}$ inch wide, extending to within $\frac{1}{2}$ an inch of the bottom of the beaker, where it is bent at right angles, the narrow corners being also bent upwards. On the bend in the metal the section of asphalt is supported, being pressed down on the sharp corners. The whole is gradually heated and kept at some convenient temperature (180° C.), and the narrow beaker placed in it. The fusing-point is taken as the point at which the softened sample just touches the bottom of the beaker on either side of the bend. A metal disc placed on the bottom of the beaker greatly facilitates removal of the specimen.

The dimensions of the apparatus used were as follows: Outside beaker, width $2\frac{1}{2}$ inches, height $3\frac{1}{2}$ inches; inside beaker, width $1\frac{3}{8}$ inches, height $4\frac{1}{8}$ inches; length of lower bend of support $\frac{5}{8}$ inch; width of metal support $\frac{1}{2}$ inch; distance of specimen from false bottom of beaker $\frac{1}{2}$ inch; distance of thermometer from specimen $\frac{1}{8}$ inch; size of specimen 1 by $\frac{1}{2}$ by $\frac{1}{8}$ inch. The last four dimensions must evidently always be kept constant. Results obtained with this apparatus do not vary more than 2° or 3° at most, and generally there is no variation. A. G. L.



The Heat Test for Explosives. W. Cullen. (*Journ. Soc. Chem. Ind.*, 1901, xx., 8.)—The frequent irregularities in the results given by the heat test for explosives are due in great measure to the use of different grades of paper to carry the starch and potassium iodide reagents on which the test depends. Moreover, even with one particular make of paper sensitiveness diminishes with age, especially during the first six weeks after the material is prepared; but from that date onwards its indications become much more constant. Cullen therefore suggests that some arrangement should be come to among manufacturers and others to use only one kind of paper (as is done by the War Office), and to have it prepared in batches sufficient to last several years by some central authority. The Government paper is like ordinary thin blotting, 0.0082 inch thick on an average, and weighing in the air-dry state 75 grammes per

square metre. As an alternative he proposes—and the desirability of this was emphasized by speakers in the subsequent discussion—to seek some substance other than paper to carry the reagents, thus avoiding the presence of adventitious matter which may affect the indications of the test. F. H. L.

Fluorescein as an Indicator. H. Zellner. (*Pharm. Zeit.*, 1901, xlvii., 100; through *Chem. Zeit. Rep.*, 1901, 40.)—The author strongly recommends fluorescein as an indicator, especially in determining ammonia when the reaction is extremely sharp. It is often indispensable in titrating dark or coloured liquids. Carbonates do not interfere. 0.4 gramme should be dissolved in 50 c.c. of alcohol and diluted with 30 c.c. of water. F. H. L.

INORGANIC ANALYSIS.

The Determination of Copper in Pyrites. O. N. Heidenreich. (*Zeits. anal. Chem.*, 1901, xxxiv., 15-17.)—The author recommends the use of aluminium for the separation of the copper from iron previous to electrolysis.

Cobalt, nickel and zinc, when present in small quantity, do not affect the results, since they are only partially precipitated, and are not separated by electrolysis from an acid solution. Lead is deposited as peroxide on the positive pole. When not present in too large amount it also is without influence on the results. Satisfactory figures are shown in the tables giving the results of test experiments. C. A. M.

The Separation of Arsenic. M. Rohmer. (*Berichte*, 1901, xxxiv., 33.)—Since E. Fischer based a method of separating arsenic on the volatility of its chloride (*Liebig's Ann.*, ccviii., 182), various attempts have been made to replace the ferrous chloride by another reducing agent, so as to overcome the difficulties introduced by the necessity of using so much of that salt.

Friedheim and Michaelis (*ANALYST*, xx., 235) recommended methyl alcohol, whilst Piloty and Stock (*ANALYST*, xxii., 297) distilled the arsenic in a current of hydrochloric acid gas and hydrogen sulphide. The author objects to the first method on the ground that several distillations are necessary, and to the second because the arsenic sulphide must be freed from sulphur before weighing. The method which he recommends consists in distilling the arsenical solution in a current of hydrochloric acid gas and sulphur dioxide in the presence of a small quantity of hydrobromic acid, without which, as Bunsen has shown (*Liebig's Ann.*, xcii.), the reduction is slow and often incomplete.

The solution containing the arsenic is placed in a 500 c.c. flask with a long neck, and sufficient concentrated hydrochloric acid added to fill the flask to about a third of its volume. One gramme of hydrobromic acid is then introduced (about 1.5 grammes of potassium bromide or 1 gramme of bromine and sulphurous acid).

The flask is inclined at an angle of 45° and closed with a rubber cork, through which pass the delivery tube, and a tube which reaches nearly to the bottom of the flask. The latter is connected with a T-piece, through which a rapid current of hydrochloric acid gas and a slow current of sulphur dioxide are introduced. The

delivery tube is conducted to the bottom of a litre flask containing 300 c.c. of water, which is cooled in a freezing mixture.

The distillation is continued for about forty-five minutes, until the residue is only about 40 c.c. Under these conditions, 0.15 gramme of arsenic is completely expelled by one distillation.

For a gravimetric determination the distillate is boiled for twenty minutes under a Liebig's condenser to expel the sulphur dioxide, a current of carbon dioxide being meanwhile introduced through a long tube passing through the inner tube of the cooler. The arsenic is then precipitated as sulphide, and weighed with the usual precautions.

It can also be determined volumetrically by boiling an aliquot portion of the distillate, previously diluted with twice its volume of water, in a beaker covered with a clock-glass, and, after removal of the sulphur dioxide, titrating the arsenious acid with $\frac{N}{20}$ iodine solution.

Antimony, when present, is left in the distillation flask, and can be determined as sulphide after removal of the sulphur dioxide and dilution. The precipitate can be completely freed from small quantities of sulphur by heating it for two hours at 225° to 230° C. in an atmosphere of carbon dioxide.

C. A. M.

On the Separation of Zinc from Nickel (and Cobalt). F. P. Treadwell. (*Zeit. anorg. Chem.*, xxvi., 104.)—In Zimmermann's method the zinc is precipitated from a nearly neutral solution of the chlorides, to which an excess of ammonium thiocyanate has been added, by means of hydrogen sulphide at 70° C. Experiments were carried out to see whether the ammonium thiocyanate could be replaced by other salts of strong acids. To the solution containing an amount of oxides of zinc and nickel (as sulphates or chlorides) equivalent to $\frac{1}{4}$ per cent. of the solution, 8 or 10 drops of binormal hydrochloric acid and 2 per cent. of ammonium sulphate or chloride were added, and hydrogen sulphide was then passed in to saturation at 50° C. The precipitate was filtered, washed with hydrogen sulphide water containing 2 per cent. of the ammonium salt and a few drops of mineral acid, and the zinc determined as usual. Using ammonium chloride and sulphate, the results obtained were as good as those given by ammonium thiocyanate. The separation of zinc sulphide is also stated to be complete in the presence of potassium chloride or sulphate.

A. G. L.

Detection and Estimation of Minute Quantities of Manganese. H. Marshall. (*Chem. News*, vol. lxxxiii., p. 76.)—The author finds that small quantities of manganese can be detected by gently warming the solution with potassium or ammonium persulphate (the former being generally preferable) in presence of sulphuric or nitric acid, and one drop of dilute silver nitrate solution. A pink coloration is developed, even when the final volume of liquid (about $\frac{1}{2}$ c.c.) contains only 0.001 milligramme of manganese. The reaction is apparently due to the formation and decomposition of silver peroxide derived from the persulphate. It may be utilized as a colorimetric test, the standard permanganate solution used for comparison being reduced for storage to prevent loss by deposition, and re-oxidized before use. C. S.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

WE note that the first examination in the branch of Biological Chemistry will be held at the Institute of Chemistry in October next, Professor Adrian J. Brown being the examiner. The precise date is not yet fixed. The examination is open to any candidate whose application for admission to the final examination has been accepted by the Council, and to any candidate who has passed the intermediate examination of the Institute. It will extend over at least four days, and may be theoretical, practical, written, and oral. The syllabus is as follows: Biological chemistry, with special reference to the chemistry and bacteriology of foods, water, sewage, and effluents, and the practical applications of biological chemistry to industries. Candidates presenting themselves in this or any other branch of the final examination will be expected to possess a general knowledge of all branches of chemistry, in addition to a thorough knowledge of the particular branch selected, and they must be familiar with the use of such scientific instruments as are commonly found in chemical laboratories. Any candidate for the final examination may present a thesis upon any chemical subject to which he has paid special attention, and such thesis, if approved by the examiners, may be taken as part of the examination. Candidates are also at liberty to submit note-books containing records of any work done by them which have not already been inspected by the examiners. The contents of note-books will be taken into consideration.

The course of study recommended is: A course of forty to fifty lectures on the morphology and physiology of micro-organisms. Practical work to include: (a) Microscopy, the preparation, staining, mounting, drawing, and recognition of specimens; (b) the preparation and study of pure cultures; (c) the conduct of fermentation experiments and the study of chemical changes brought about by bacteria, moulds, yeast, etc. Examinations in the branch of biological chemistry of the final examination will be held annually in October, while the examinations in the other branches will be held in January and July as heretofore.

REVIEW.

A SHORT MANUAL OF INORGANIC CHEMISTRY. By A. DUPRÉ, PH.D., and H. WILSON HAKE, PH.D. Charles Griffin and Co., London. Price 9s.

This well-known and excellent work has now reached a third edition. It has been thoroughly revised and brought up to date, and, while retaining the main features of the former editions, has undergone considerable alteration, chiefly occasioned by the arrangement of the bulk of the matter according to the periodic system of classification, and this has necessitated the rewriting of a considerable portion of the work. The general appearance of the book is to a considerable extent marred by the printing, which in places might have been much better, and does not nearly come up to the usual standard of the firm from which it emanates. W. J. S.

ERRATUM.

This vol., p. 138, line 10 from bottom, for "300 c.c." read "30 c.c."